
Corrosion and Hydriding in Nuclear Alloys Studied with Synchrotron Radiation

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Outline



Why use synchrotron radiation

Applications of synchrotron radiation to the study of corrosion and hydriding mechanisms in nuclear alloys

1. Microbeam synchrotron radiation diffraction
2. In situ studies of Phase formation
3. Bulk diffraction

Why Synchrotron Radiation?

- **Very high brilliance and photon flux** (orders of magnitude higher than conventional sources)
 - ⇒ **fast data acquisition, ability to detect small diffraction signals**
- **Energy tunable characteristics** (conventional sources are fixed energy)
 - ⇒ **use $E \sim 9$ keV -very sensitive for detecting Fe and transition elements (can detect ppm levels)**
 - ⇒ **use high energy (80 keV) to penetrate 1 mm sample in transmission (bulk diffraction); can also measure texture.**

Advanced Photon Source
Synchrotron Facility at
ANL



Why Synchrotron Radiation? (2)

- In a particular beamline at the APS (2ID-D) **can focus x-ray beam to 0.25 μm spot => microbeam synchrotron radiation diffraction**
 - ⇒ combination of **high spatial resolution** and high elemental sensitivity can determine crystal structure at this scale
- Low background, very sharp peaks
 - ⇒ **precise structure determination**
 - ⇒ **ability to detect small volume fractions of second phases (as low as 0.1%)**
- **At APS=> In situ loading and temperature variation (1ID); precise detection instruments and software.**
- **Other techniques allow to study chemical state of materials etc. => not reviewed here**



Applications

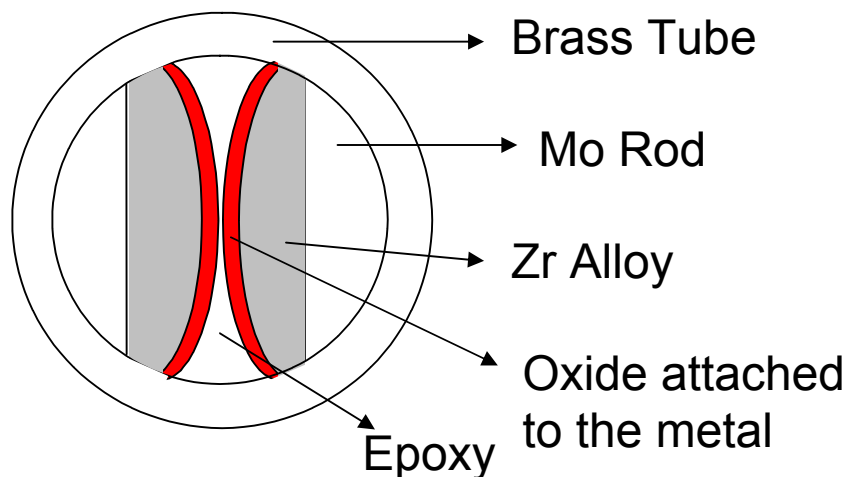
1. Microbeam synchrotron radiation diffraction and fluorescence studies of oxide layer structure
2. In situ studies of Phase formation and reorientation performed in transmission (load and temperature)
3. Bulk diffraction studies of second phases

1. Microbeam synchrotron radiation diffraction and fluorescence studies of oxide layer structure

- **Issue: Can we understand differences in alloy corrosion behavior through the structure of their protective oxides**
- **Expose samples to form oxide layers in different environments for different times.**
- **Prepare cross sectional sample, examine with microbeam (0.2 μm), can obtain in a spatially resolved manner the phases present, grain size, texture, etc. (all diffraction information) in parallel with fluorescence.**
- **Examined Zr alloy oxides (360°C and 500°C) and ferritic-martensitic alloys (500 and 600°C)**

Cross-sectional Oxide Sample preparation

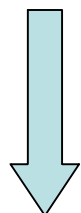
μ -XRD and μ -XRF



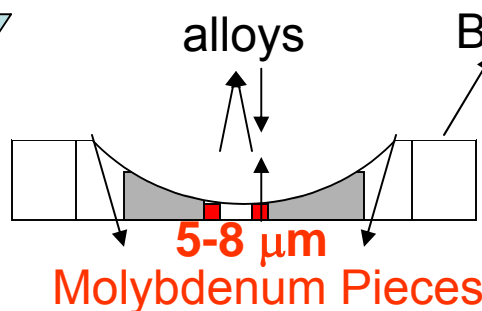
Look along axis of tube in x-section

Same samples used for the different techniques (at various stages of preparation)

dimple



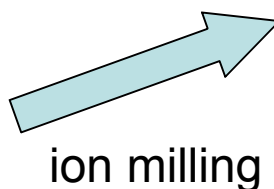
Oxides attached to Zr-based alloys



Transmitted Light Optical Microscopy

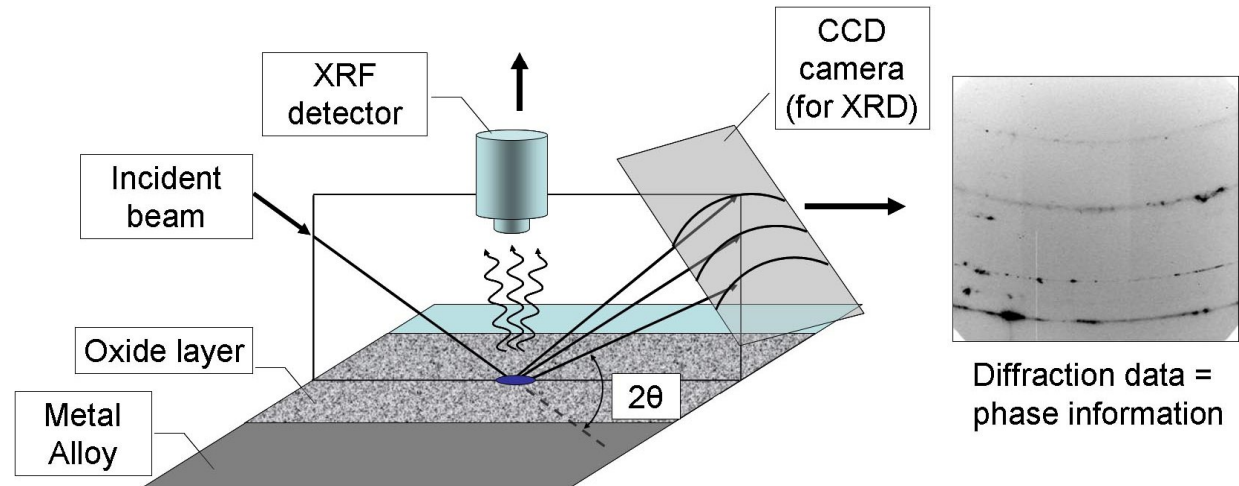
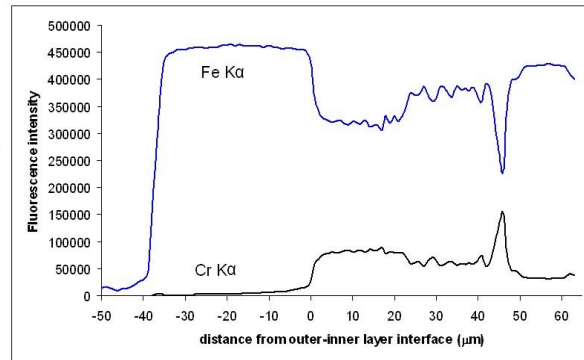
Cross-sectional **TEM**

Examined in Philips CM-30 at W and Philips 420 at PSU



Microbeam Synchrotron Radiation Diffraction and Fluorescence

Fluorescence
data =
elemental
information

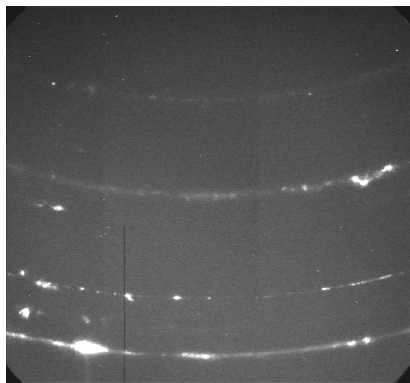


Focused beam 0.2 μm step size, and scan step by step through oxide layer

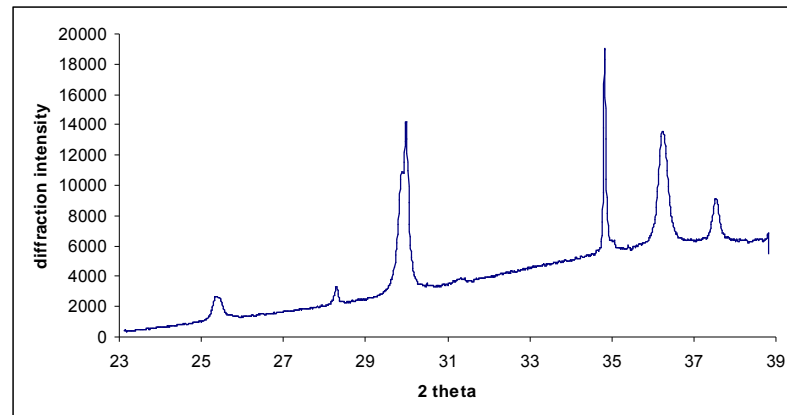
Simultaneous fluorescence + diffraction acquisition = elemental + phase information

Can differentiate between similar phases (e.g. Fe_3O_4 and FeCr_2O_4)

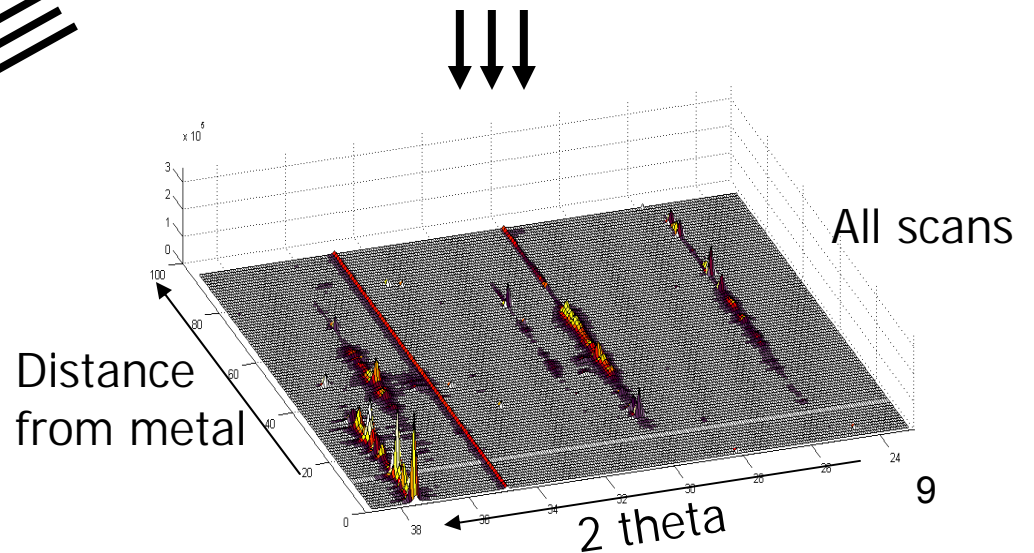
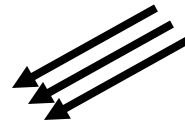
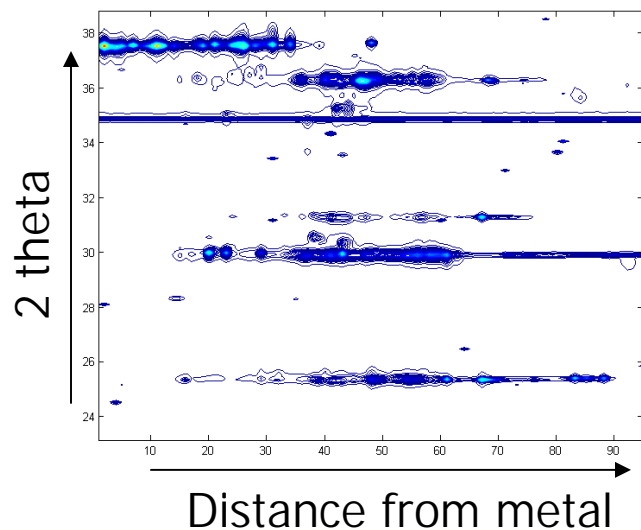
Compile all the scans to create diffraction maps
giving phases as a function of distance



integration



1 scan

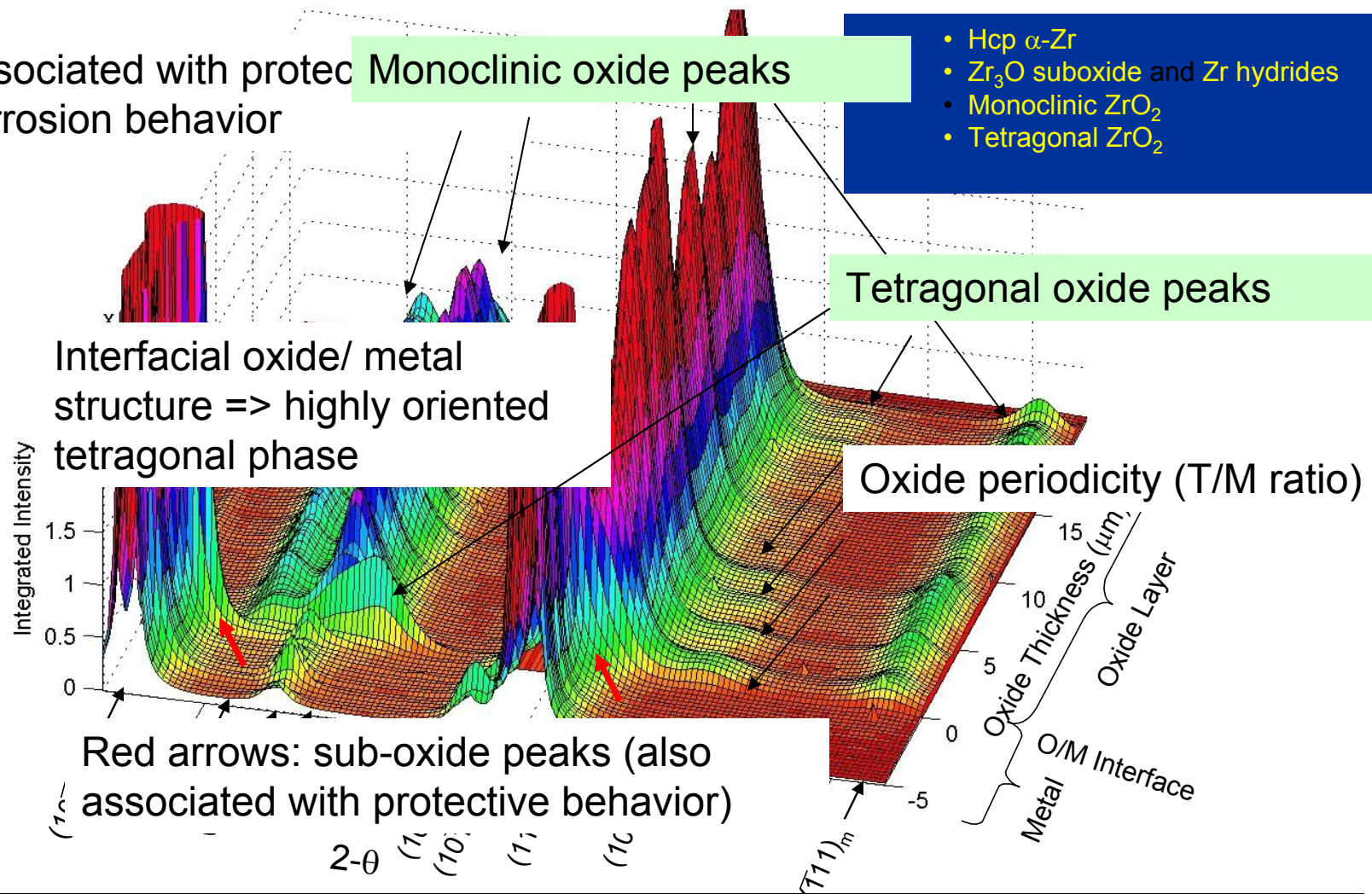


Oxide Layers in Zirconium Alloys (ZIRLO)

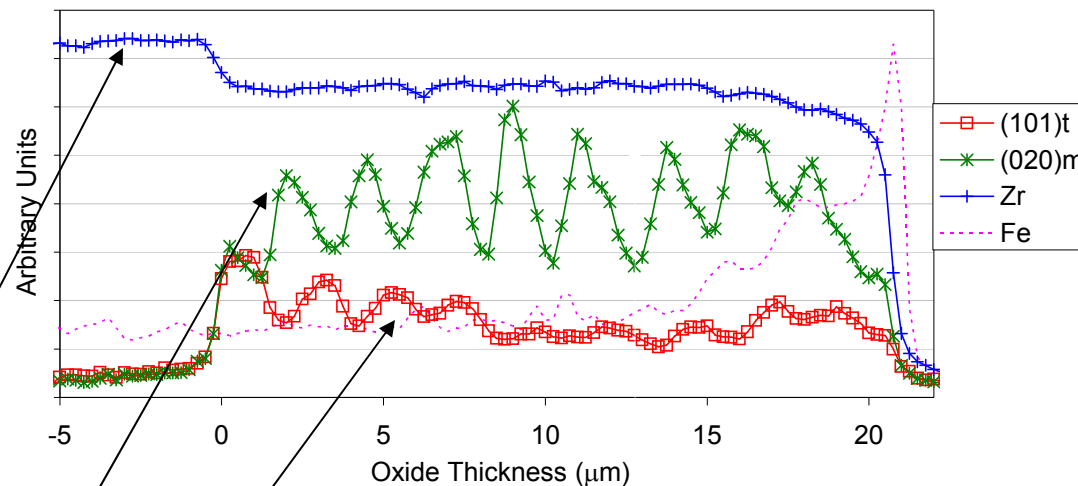
ZIRLO in 360 C pure water, ~ 20 micron oxide

Associated with protective corrosion behavior

- Hcp α -Zr
- Zr_3O suboxide and Zr hydrides
- Monoclinic ZrO_2
- Tetragonal ZrO_2



Diffraction peak Periodic Intensity Variation => shows phase variation



- Zr fluorescence line allows us to locate the oxide layer
- **(020)_m peak** intensity changes periodically across the oxide layer because of the texture gradient
- **(101)_t peak** has similar periodicity as **(020)_m peak** but they are out of phase with each other
- Beamline 2ID-D's small beam much smaller than others (normal size for small beam is about 1 μm, whereas they have 0.2 μm)

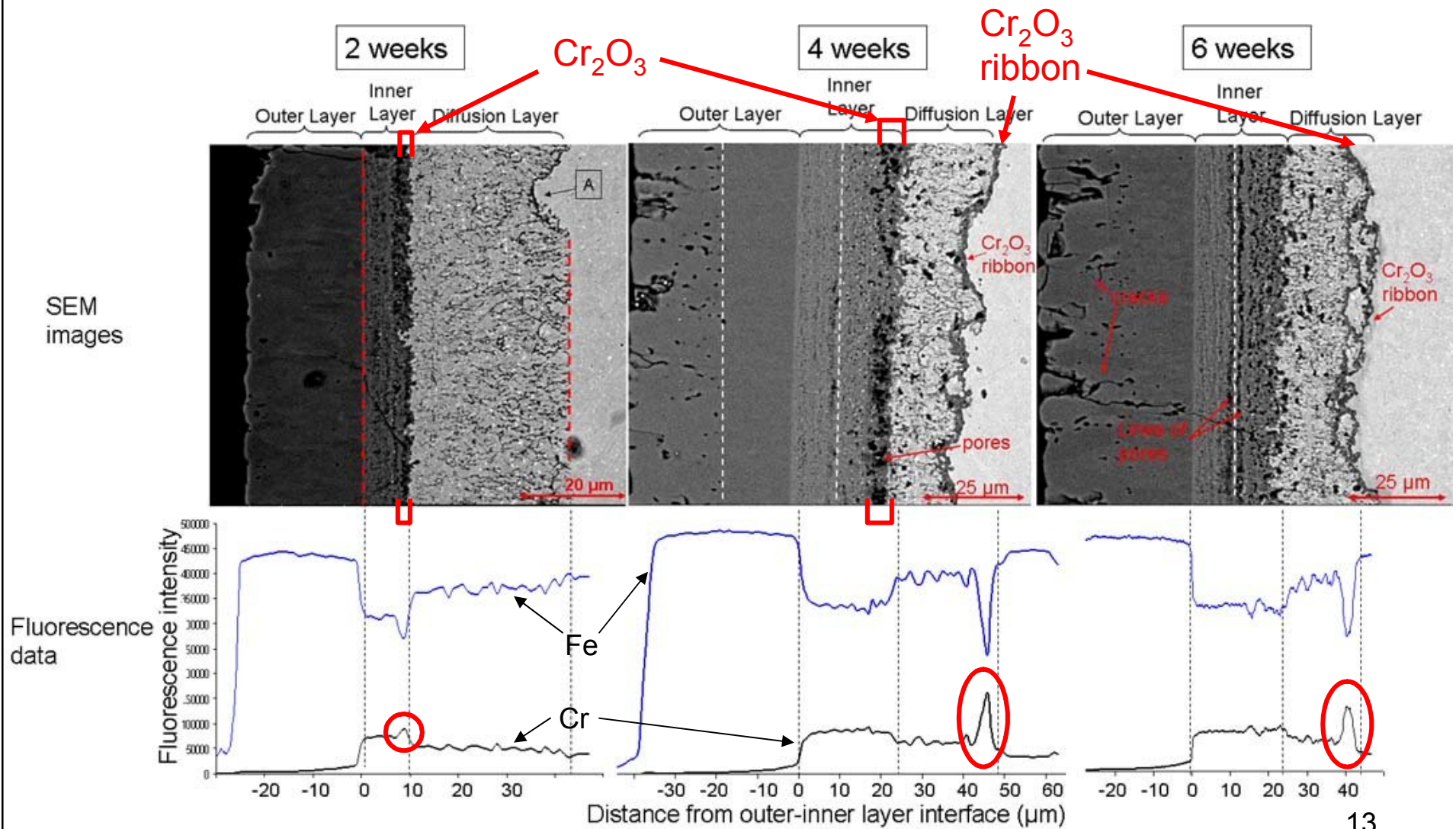
Oxide layers in Zr Alloys

1. A **clear correlation** was found between **oxide-metal interfacial microstructure and protective nature of the oxide** (when interfacial structure present, oxide is protective, when it is not present, it is not protective).
2. Same oxide layers were studied in oxides formed at 500°C in supercritical water and similar oxide phases and oxide-metal interfacial structures were observed in protective and non-protective oxides*
3. Model proposed ** to correlate alloy microstructure with protective oxide microstructure.

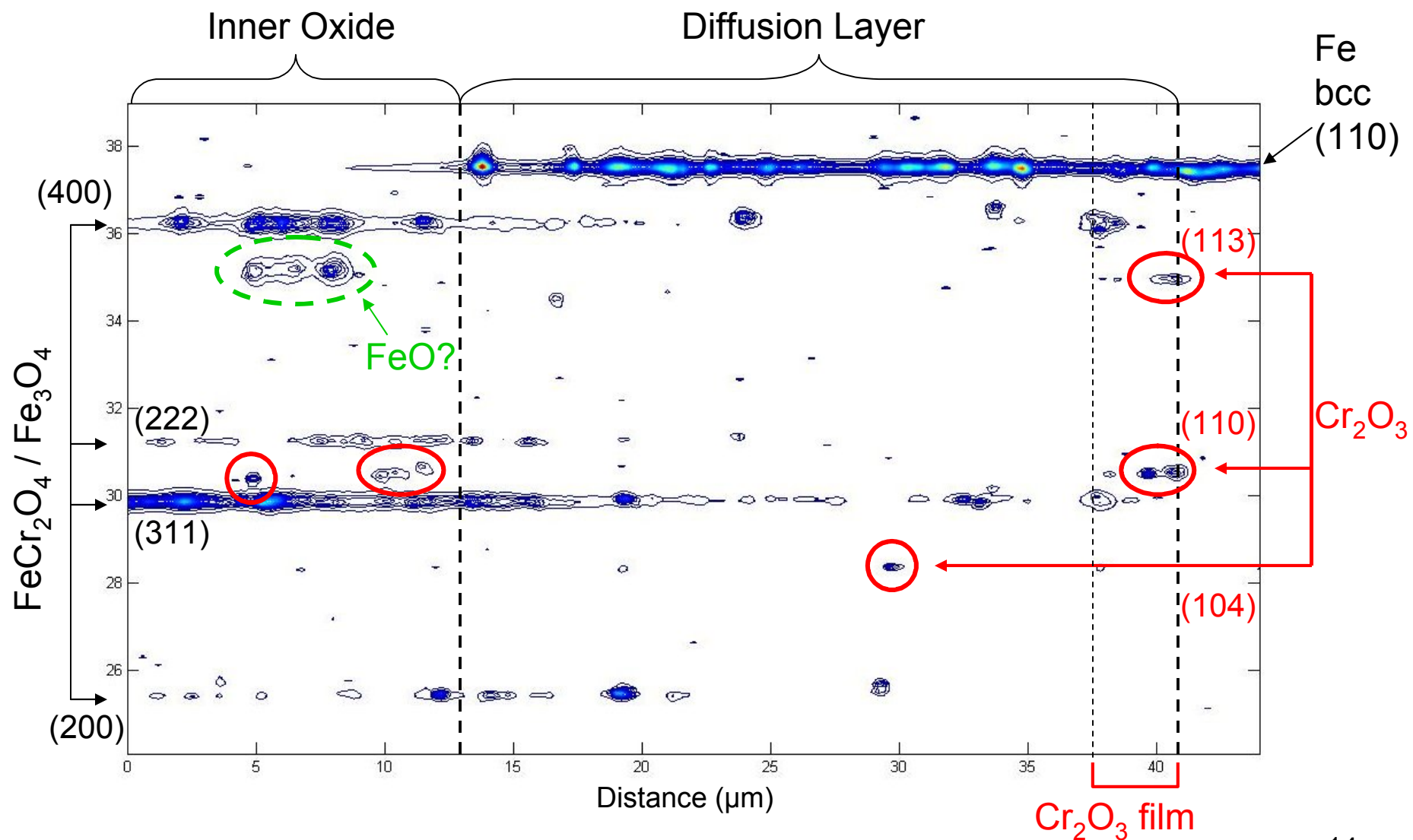
*A. Motta, A. Yilmazbayhan, M. Gomes da Silva, R. J. Comstock, G. Was, J. Busby, E. Gartner, Q. Peng, Y. H. Jeong, and J. Y. Park, "Zirconium Alloys for Supercritical Water Reactor Applications: Challenges and Possibilities," *Journal of Nuclear Materials* 371 (2007) 61-75.

**A. T. Motta, A. Yilmazbayhan, R. J. Comstock, J. Partezana, G. P. Sabol, Z. Cai., and B. Lai, "Microstructure and Growth Mechanism of Oxide Layers Formed in Zr Alloys Studied with Micro Beam Synchrotron Radiation," *Journal of ASTM International* 2 (2005) Paper # JAI 12375.

Oxide layers in Ferritic-martensitic Steels (e.g. 9CrODS, 600C)



Diffraction data contour plot



Oxide layers in 9 Cr ODS*

- Clearly identified Cr_2O_3 oxide layer forming during corrosion process. Also FeCr_2O_4 appears in layers near interfaces. Such phases are associated with protective behavior
- Detailed process of phase formation within the three oxide sub-layers could be studied and compared to both corrosion kinetics (weighting measurements) and to TEM studies of oxide microstructure.
 - J. Bischoff, A.T. Motta, Y. Chen, T. R. Allen, "Oxidation of 9CrODS Exposed to Supercritical Water," Proceedings of the NACE 2009 Corrosion Conference, Atlanta, paper # 09248.
 - Jeremy Bischoff, Arthur T. Motta, Robert J. Comstock, "Evolution of the Oxide Structure of 9CrODS Exposed to Supercritical Water," Journal of Nuclear Materials, in press 2009.
 - Jeremy Bischoff, Arthur T. Motta, Lizhen Tan and Todd R. Allen, "Influence of Alloy Microstructure on Oxide Growth in HCM12A in Supercritical Water", Materials Research Society (MRS) Proceedings Symposium R: Materials for Future Fusion and Fission Technologies, 2008, paper ID R # 519941

2. Kinetics of zirconium hydride dissolution and precipitation near a crack tip



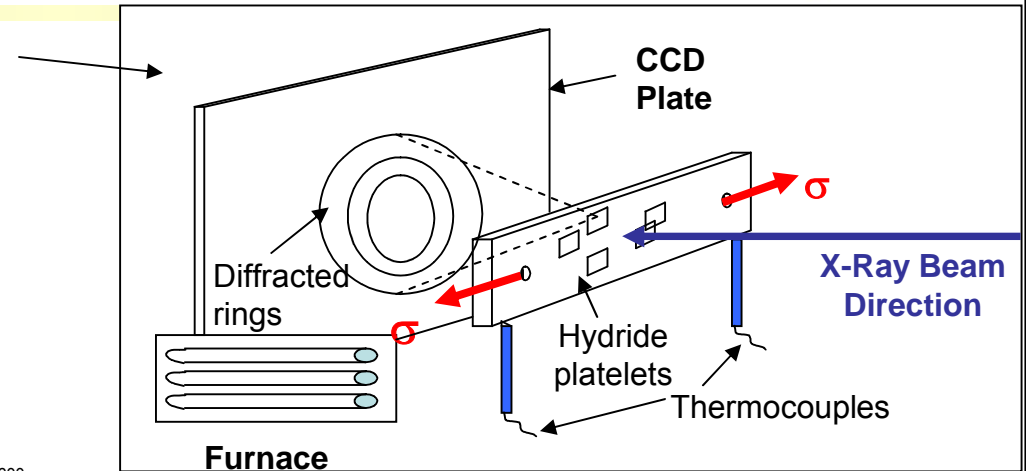
- Issue: Hydrogen ingress into Zr alloys during corrosion, precipitates as hydrides
 - Hydrogen in solid solution can respond to temperature and stress gradients and precipitate near a crack tip => delayed hydride cracking (DHC). DHC studies are performed post facto (after cooldown) and have to infer hydride microstructure at high temperature.
- => Study processes of hydride dissolution and precipitation near a crack tip in situ using synchrotron radiation diffraction (under load and at temperature)

Kinetics of zirconium hydride dissolution and precipitation studied using synchrotron radiation

- In-situ transmission X-Ray diffraction experiment at beamline 1-ID

Analysis of diffraction data shows

111 peak intensity of hydride particles initially the same

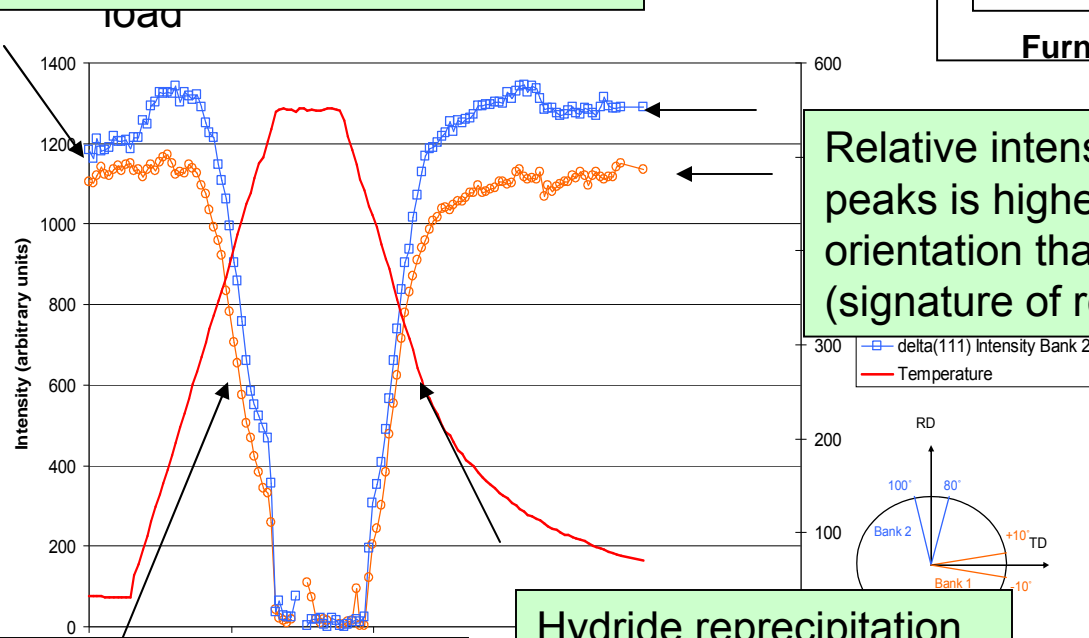


Experimental set-up

Relative intensity of 111 hydrides peaks is higher in 12'o clock orientation than at 3 o'clock (signature of reorientation)

of hydrogen

solubility limit in zirconium

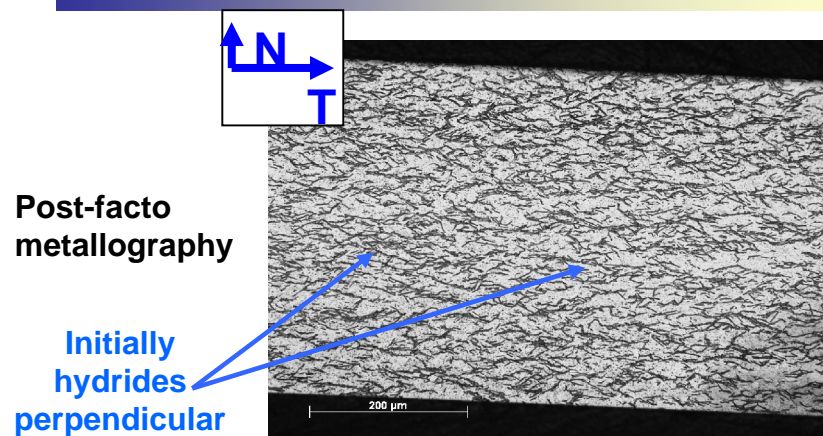


Hydride dissolution as T increases

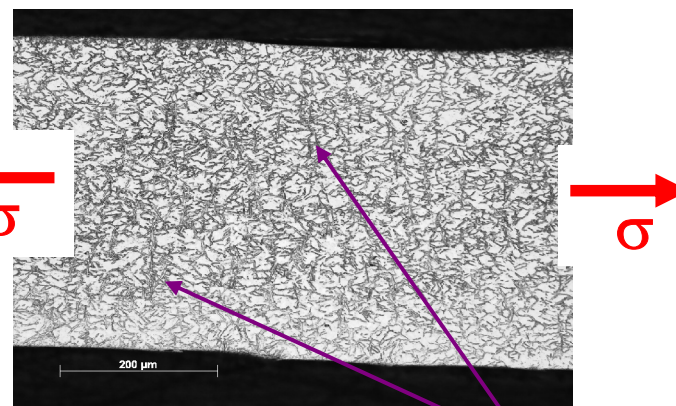
Hydride reprecipitation as T decreases

- Information on evolution of hydride precipitation (what hydride precipitate first, in what shape)
- Texture information by integrating rings over different directions

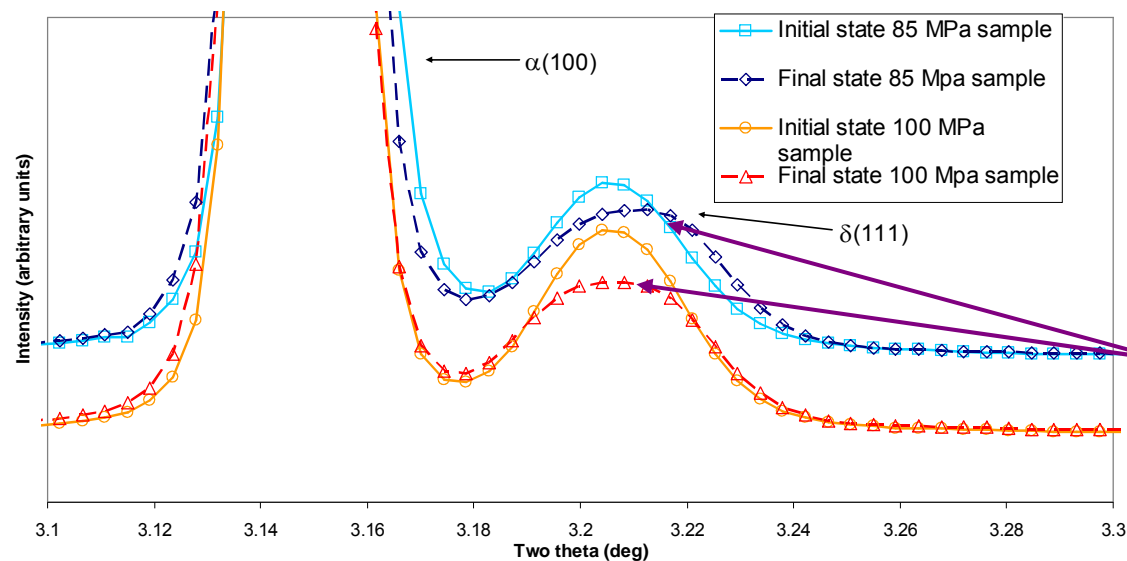
Kinetics of zirconium hydride dissolution and precipitation studied using synchrotron radiation



85 MPa
Reorientation



- Observation of hydride reorientation under tensile loading (correlation of diffraction patterns with post-facto metallography)

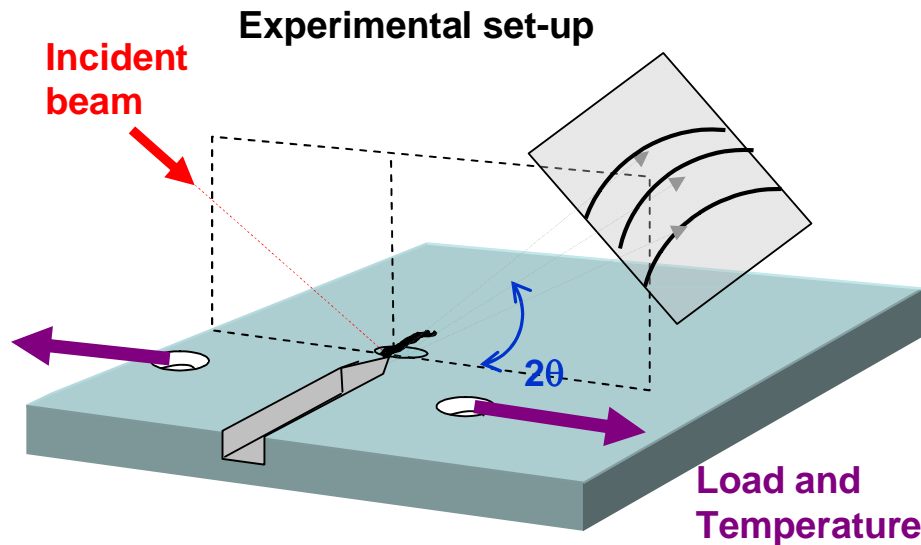


Diffracted peaks of reoriented hydrides are wider

In-situ transmission X-Ray diffraction patterns

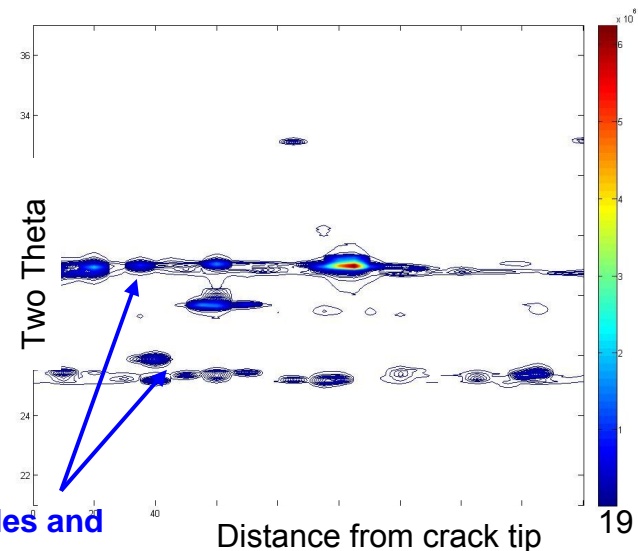
Kinetics of zirconium hydride dissolution and precipitation studied using synchrotron radiation

- Future experiment goal: micro-beam observation of crack-tip in zirconium under loading and heating at beamline 2-IDD
 - Observe hydride formation at the crack tip while under load and temperature. Determine kinetics of hydride precipitation. Possibly observe evolution of damage and fracture event.



Observation of hydrides and matrix peaks

Preliminary results at room temperature with no load in a cracked sample with hydrides at the tin



3. Bulk Diffraction determination of Second phases

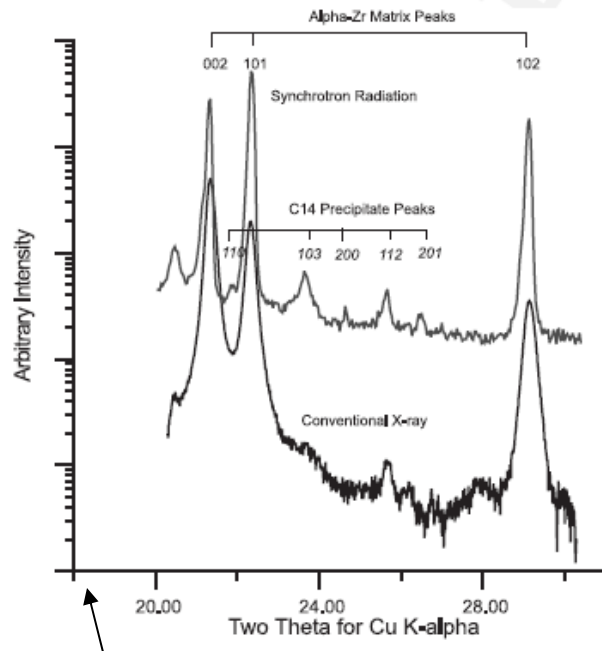
- Performed in theta-2theta configuration (most similar to conventional XRD)
- Able to detect very small levels of second phases (depending on structure factors, 0.1-0.5%)
- Data has low background, and high signal to noise ratio, beam broadening is quite small.
- High energy allows probing very large number of second phase particles

Precipitates in Zircaloy-4 *

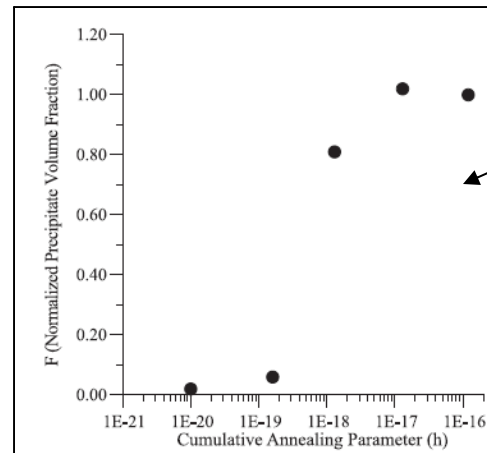
- Issue: Corrosion properties in zirconium alloys depend strongly on the distribution, structure and size of second phase particles.
- Difficult to study with conventional XRD and TEM studies are normally not representative (exclude small sizes, not enough volume, have to count many particles, etc.)
- Can study using synchrotron radiation diffraction and count precipitation right from when it starts

* Erwin, K. T., Delaire, O., Motta, A. T., Birtcher, R. C., Chu, Y., and Mancini, D., "Observation of Second Phase Particles in bulk Zirconium Alloys Using Synchrotron Radiation," Journal of Nuclear Materials, 294, (2001) 299-304.

Precipitates in Zircaloy-4 *



Synchrotron radiation diffraction x-ray diffraction generates superior data to conventional XRD

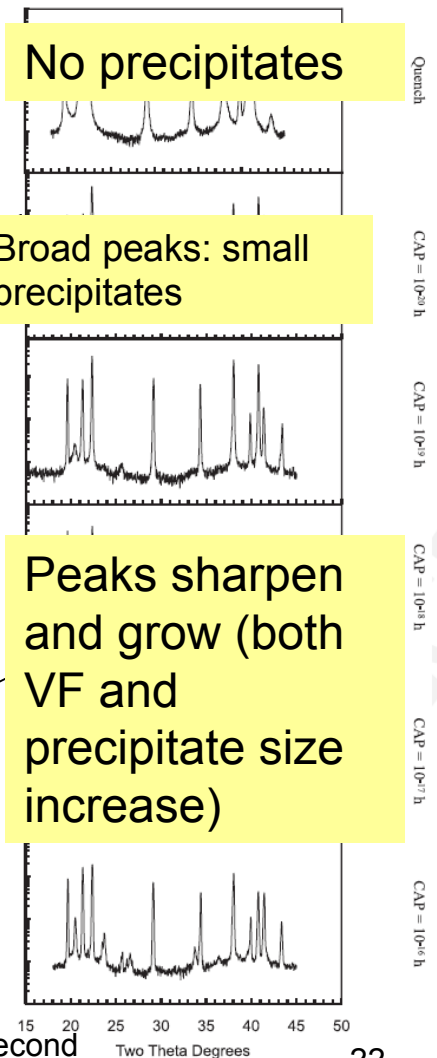


Precipitate volume fraction evolution can be clearly seen as a function of annealing parameter

No precipitates

Broad peaks: small precipitates

Peaks sharpen and grow (both VF and precipitate size increase)

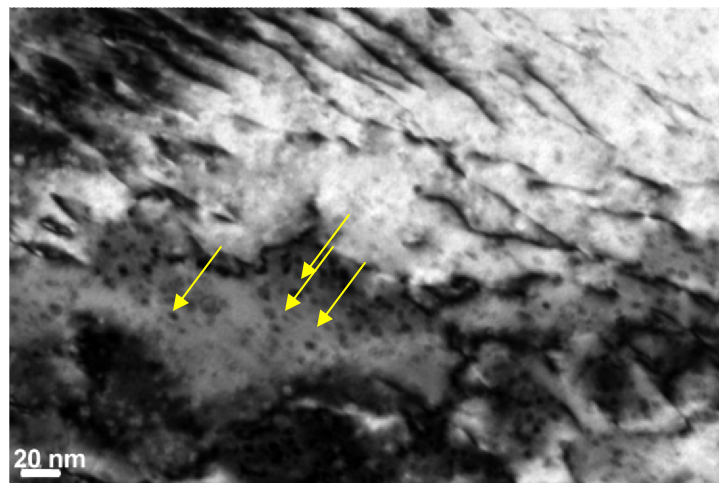
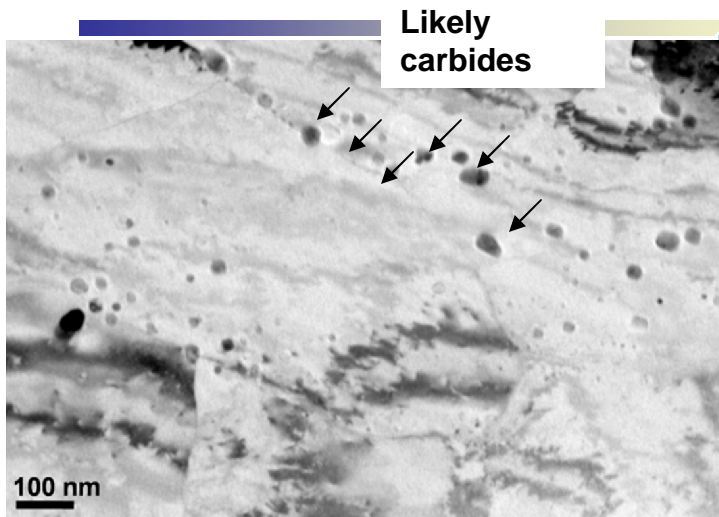


* Erwin, K. T., Delaire, O., Motta, A. T., Birtcher, R. C., Chu, Y., and Mancini, D., "Observation of Second Phase Particles in bulk Zirconium Alloys Using Synchrotron Radiation," Journal of Nuclear Materials, 294, (2001) 299-304.

18Cr ODS CEA*

*Kaoumi et.al., presentation at Symposium R,
MRS Fall Meeting 2008

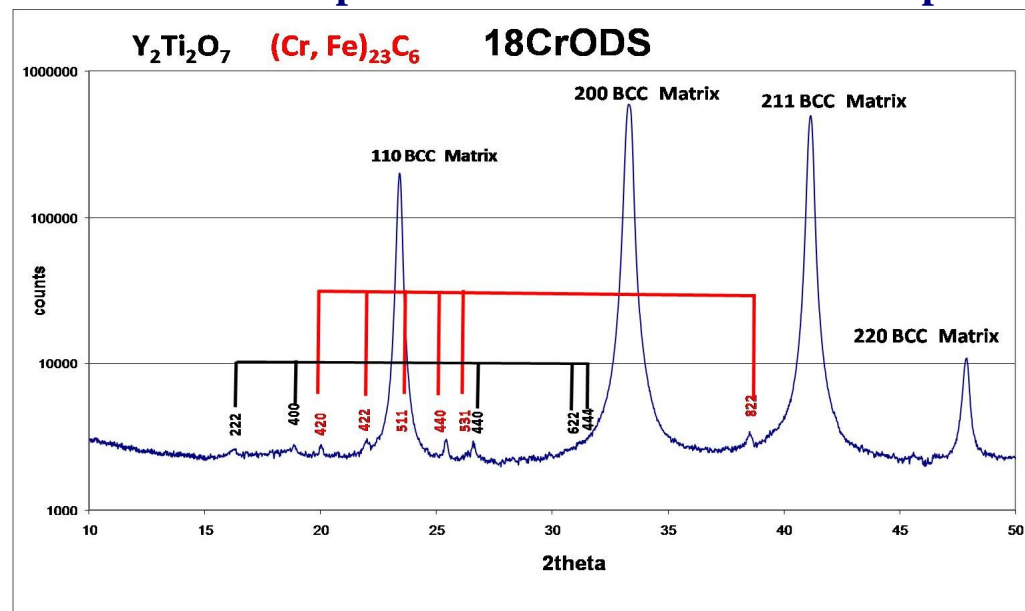
PENNSTATE



Composition
(CEA
analysis)

**Fe-18Cr-1W-0.25Ti-0.3Mn-0.3Si-
0.19Ni-0.027C-0.11O-0.56 Y₂O₃**

- Second phase particles:
- Y₂Ti₂O₇ oxides and **Cr rich carbides (Cr, Fe)₂₃C₆**;
- No Y₂O₃ signal
- bcc matrix cell parameter: 2.88Å vs. 2.8664 for pure Fe.



Oxides dissolve during mechanical alloying process and nano-oxide clusters have reprecipitated during the hot isostatic phase of the alloy processing. 23

Conclusions

- Synchrotron radiation diffraction and fluorescence is a powerful technique for materials characterization that can provide unique information
- Possibilities to combine with high spatial resolution to obtain local information using microbeam.
- Can also perform in situ work (under load and at temperature) also can perform in situ corrosion.
- Other possibilities not discussed include studying stress accumulation, gradients, and studying chemical state of materials.
- APS provides a great environment to use synchrotron radiation

Researchers and Funding

at PSU

Aylin Yilmazbayhan
Ken Erwin
Olivier Delaire
Robert Daum
Jeremy Bischoff
Marcelo Gomes da Silva
Kimberly Colas
Robert Comstock (W)
Djamel Kaoumi
Jamie Kunkle
Cem Topbasi

at APS

Barry Lai
Zhonghou Cai
Joerg Maser
Yong Chu
Jan Ilavsky
Jon Almer
D. Mancini

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END

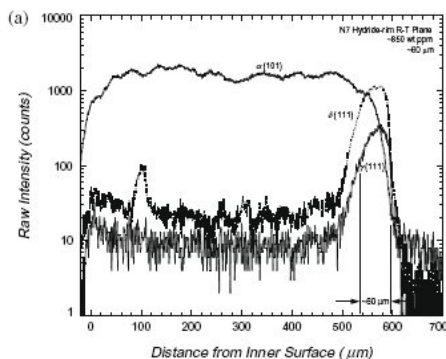
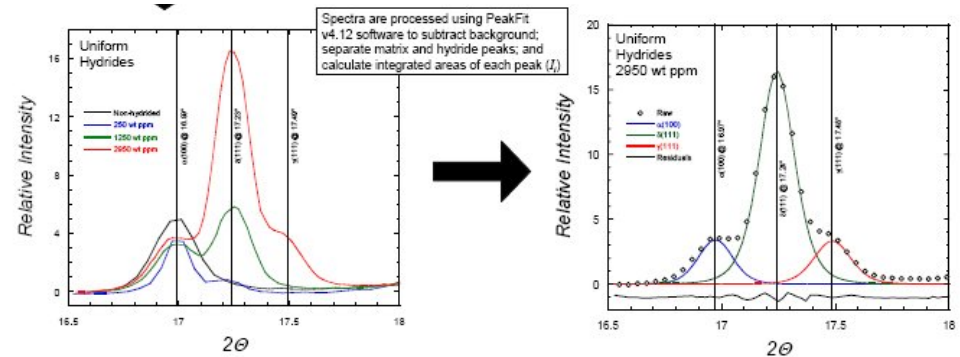
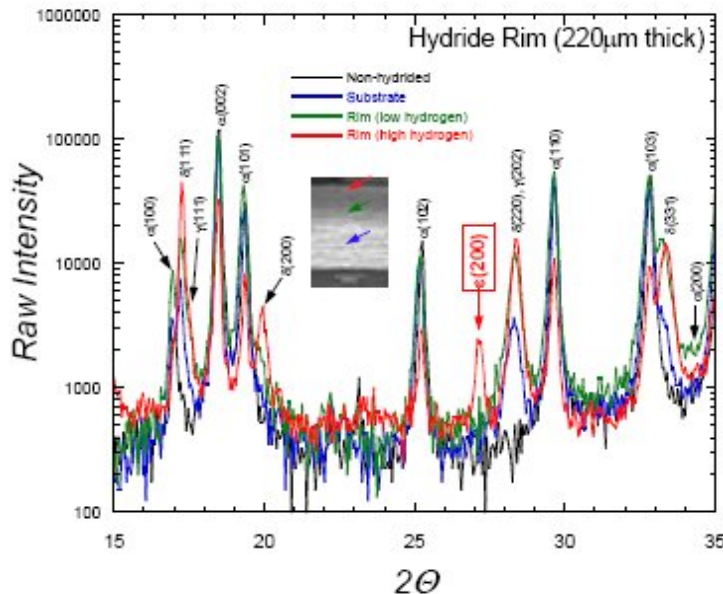
atm2@psu.edu

Hydrides in Zircaloy-4 *

- Issue: Hydrides formed during corrosion severely impact cladding ductility during a reactivity initiated accident
 - Both hydrogen content and hydride distribution are important. In particular the presence of a hydride rim (formed under the influence of a temperature gradient) is detrimental to cladding.
 - Difficult to measure local hydrogen concentration (LECO analysis requires large volumes and metallography has errors associated with etching)
- => Can measure hydrogen content using x-ray diffraction (both bulk and “micro” beam)

* Robert S. Daum, Yong S. Chu and Arthur T. Motta, “Identification and Quantification of hydride phases in Zircaloy-4 cladding using Synchrotron radiation Diffraction,” Journal of Nuclear Materials, in press, 2009.

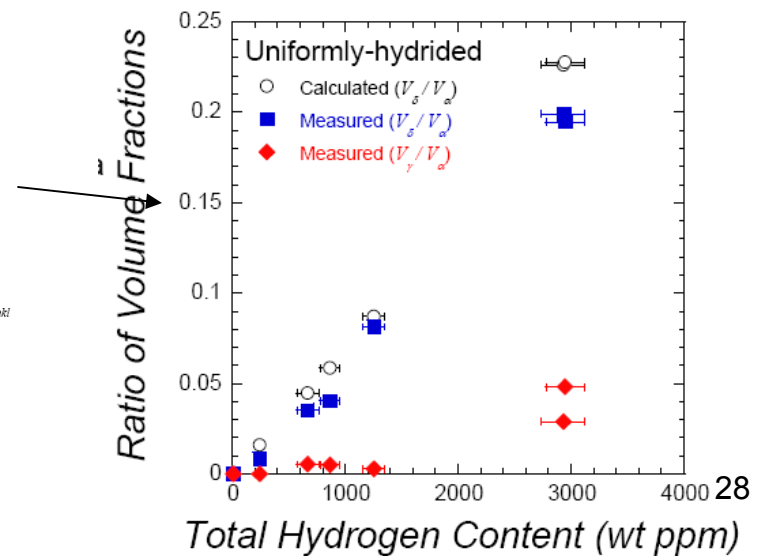
Hydride Diffraction in Zr alloys



$$\frac{I_{\gamma(111)}}{I_{\alpha(002)}} = \frac{R'_{\gamma(111)}V_{\gamma}}{R'_{\alpha(002)}V_{\alpha}} \quad \frac{I_{\delta(111)}}{I_{\alpha(002)}} = \frac{R'_{\delta(111)}V_{\delta}}{R'_{\alpha(002)}V_{\alpha}}$$

where

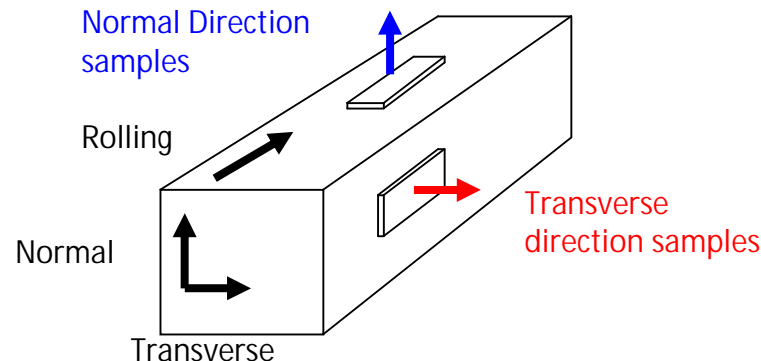
$$R'_{hkl} = \left(\frac{1}{v^2} \right) \left[F_{hkl}^2 P_{hkl} \left(\frac{1}{\sin^2 \theta_{hkl} \cos \theta_{hkl}} \right) \right] (e^{-2M})_{hkl}$$



Sample Preparation for hydrided zirconium



1. Textured Zircaloy-2 or Zircaloy-4 is obtained and cut in preferential directions



2. Hydriding process:

- a. The native oxide layer is removed by dipping the sample in acid solution (10 parts Nitric Acid, 10 parts water, 1 part HF)
- b. The sample surface is coated with a 200 Angstroms thick Ni surface by electron gun deposition
- c. The samples are put into a vacuum furnace where Argon and Hydrogen gases are inserted
- d. The furnace is heated up to 450C (to prevent any recrystallization this is the maximum temperature allowed) and several heating/cooling cycles are performed with hydrogen gas inside the furnace

3. Checking the process worked: metallography or hot vacuum extraction are performed to check the sample has taken hydrogen